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Determination of Toxic Heavy Metals in Atmosphere of Kalar, As Sulaymaniyah, Iraq

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Abstract:

Estimation of heavy metals in ambient air is crucial for environment study due to their toxicity impact on people. Some metals have been reported as carcinogenic such as arsenic (As), [hexavalent chromium (Cr), nickel and (Ni) cadmium (Cd)]. In Iraq, a lot of private electrical generators have been installed in every neighborhood of all Iraqi cities. Concurrently the industrial is so near to the population cities. This makes an uncontrolled and fearful environment. Thus the aim of this study is to find the concentration of toxic heavy metals (Pb, Cd, Hg, As, Cr, and Zn) in the air from different sites (population areas that contain many electrical generators, Industrial areas, traffic lights and green land area) in the Kalar city. Using a homemade apparatus that has a capacity of flow rate was 0.05 m^3/sec. for one hour, the total volume of each sample was 180 m^3/h collected. For this purpose, inductive coupled plasma optical emission spectroscopy (ICP-OES) has been used to determine mentioned metals, the concentration ranged from 7 μgL^{-1} - 18.5 μgL^{-1} Pb, 47 μgL^{-1} - 245 µg.m-3 Zn, 7 µg.m-3 $^{-1}$, and 13 μgL^{-1} - 106 μgL^{-1} Cr. The main sources of these heavy metals in the sampled area could be attributed to the car and electrical generation emission, and factory emission.

Keywords: *Electrical Generator, Heavy Metals, Environment, Health and ICP-OES.*

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Introduction

Generally, the industrial activities of man and the uncontrolled development of large cities during the recent past, and in Iraq especially because of a shortage of electricity after 1991, the use of private electrical generators has spread to reduce power outages. Generally, private generators are installed in neighbourhoods and city centres as there is no available place free for them in street or neighbourhood, without being bound by environmental standards. So as a result, it has been a source of contamination for soil, water, and air. Burning or combustion of fuels contributes produce smoke including toxic substances resulting from the fuel combustion **(Sawidis *et al*., 1995; Al_Saadi *et al*, 2021).**

Metal-PM can travel over a long distance upon release into the air and can deposit on the water, soil, buildings, and plant canopy. Herein, these metal-PMs can affect the ecosystem by contamination. Moreover, metal-PMs can induce several health effects when they are directly inhaled by humans as shown in Figure No. 1 **(Shahid *et al*., 2019).**

The International Agency for Research on Cancer (IARC) has classified heavy metals into three categories based on their studies on the carcinogenicity of these metals in humans. Group 1 metals and/or metalloids are proven carcinogens to humans. Group 2A compounds are probable carcinogens and group 2B compounds are possible carcinogens. Group 3 compounds are non-carcinogens to humans. Regarding the carcinogenic nature of heavy metals and/or metalloids, and their compounds, Cd and its compounds, hexavalent Cr and metallic Ni and its compounds are group 1 carcinogens for humans through the inhalation and ingestion routes of exposure and are associated with cancers of the lung, liver, nose, and kidney **(International Agency for Research on Cancer, 1987).**

Inorganic Pb compounds **(The International Agency for Research on Cancer, 2006)** are listed as group 2A, with metallic Pb **(International Agency for Research on Cancer, 2012)** and methyl mercury listed as group 2B carcinogens. Metallic Cr, trivalent Cr, metallic Hg, and organic Pb compounds are listed as group 3 compounds **(Suvarapu and Baek, 2016).**

A wide range of heavy metals and metalloids was determined by different techniques and different instruments in the atmosphere **(Najib *et al*., 2006; Kemp, 2002; Barbante *et al*., 2004)**

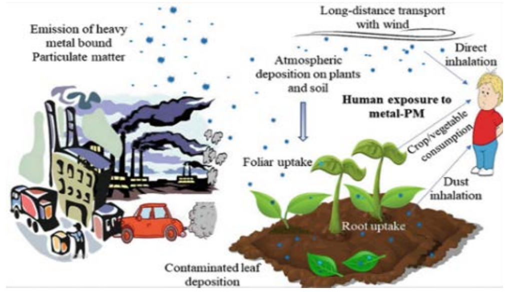

Figure No. 1: Heavy Metal (loid) – enriched particulate matter (metal-PM) released from various sources into the Atmosphere and deposition on different Terrestrial Ecosystems (soil, water, plant, and animals/human).

Thus the aim of this study is to measure the concentration of toxic heavy metals [lead (Pb), cadmium (Cd), Arsenic (As), chromium (Cr), and zinc (Zn)] in the atmosphere from different sites (population areas that contains a lot of electrical generators, Industrial area, traffic lights, and green land area)in the Kalar city As Sulaimany, Iraq.

The Standard of Air Quality

Recently, air pollution becomes more critical because of electrical generators and Industries. Iraq does not have its standard set for heavy metals concentration in the ambient air, but references such as World Organization Health (WHO), Ambient Air Quality Criteria Act 1994 (AAQC), Texas Commission on Environmental Quality (TCEQ), National Environment Protection Council (NEPS), have been being used as shown in Table 1 **(Othman, 2015).**

Table No. 1: The Standard Set for Heavy Metals in Air

Element	Concentration [$\mu g.L^{-1}$]	References
Cd	0.005	WHO, AAQC
Pb	0.500	NEPC, AAQC
Cr	0.010	TCEQ
Hg	0.0015	TCEQ
Zn	1000	EQA

Materials and Methods

Following are the material methods as performed for the study:

Sampling

Using homemade equipment by using air vacuum pump flow rate (0.05m3 /s) and ashless filter paper. A total of 14 ambient are collected from Kalar city in Industrial area, traffic lights, near from electrical generator in neighbourhoods and city centers, green land and city Centre crowded of cars.

Sample Preparation

The air samples were collected on a 9 cm diameter ashless filter. They were 0.32 mm thick, with particle retention of 1.5 pm they were weighed before and after sampling. The average air volume sampled 180 m3/h at a flow rate of 0.05 m3/s the details of the ambient air sampling can be found elsewhere. Each filter sample accurately was placed in a porcelain crucible followed by 10 ml of ultra-purified water and ashed at 700° C for 3 hours. Ashes were digested using a 5 ml of HNO3 (conc.) then diluted with Deionized water to 25 ml volume. Finally the concentration of heavy metals determined using ICP-OES.

Reagents and Chemicals

All chemicals and reagents are used were analytical reagent grade such as Nitric acid (65%) are supplied by Avonchem (Germany). An aliquot of an ICP multi-element standard solution (1000 µg.L-1Avonchem CRM).

Instrumentation

The spectral emission measurements were accomplished by Inductive coupled plasma – optical emission spectroscopy (ICP-OES) from Arcos-Spectro – Germany, Table 2 show the specification of it, Ultra-pure water deionizer and Furnace from Thermos- Germany.

Table No. 2: The Characterization of the ICP-OES

Generator Data	
Plasma Power	1400 [W]
Coolant Flow	13,00 [L/min]
Auxiliary Flow	1.00 [L/min]
Nebulizer Flow	0.83 [L/min]
Add. Flow	0.00 [L/min]
Heating	0
Torch Position X	0.0 [Min]
Torch Position Y	0.0 [Min]
Torch Position Z	10.0 [Min]

Calibration

For the preparation of calibration solution, An aliquot of an ICP multi-element standard solution (1000 µg.m-3 Chem Lab CRM) was used. The working standard solution was obtained by dilution of the stock standard solutions to desired concentration in 1% HNO3. The calibration curves range selected by (5 points) for all the elements. All correlation coefficient r2 achieved was 0.9999 as revealed in table 3. Measuring the detection limits (LOD) depended on the elemental concentrations that gave the standard deviation of a series of three blank solutions measurements.

Table No. 3: Characteristics Data of the Calibration Curves of Elements using ICP-OES

Elements	Equation	R^2	Wave length (nm)	Linear Range ($\mu g.L^{-1}$)	DL ($\mu g.L^{-1}$)	QL ($\mu g.L^{-1}$)
Zn	y = 199.98x + 74.4	0.99999	213.656	1.089-6000	1.089	3.6
Pb	y = 15.105x + 6200.6	0.99979	220.353	2.140-10000	2.140	7.1
Cd	y = 199.99x + 67.5	0.99999	214.438	12.04-10000	12.04	40.1
As	y = 12.441x + 2508.5	0.99991	189.042	51.01-5000	51.01	170.0
Cr	y = 12.37x + 3440	0.99995	267.716	15.04-5000	15.04	50.1

Results and Discussion

In this study, ten elements have been determined for 14 air samples of Kalar city. Heavy metals in the air according to WHO, AAQC, NEPC, TCEQ, and EQA. The concentration limit of mercury, lead, zinc, hexavalent chromium, and cadmium is determined as present in Table No. 1. Table No. 4 presents a summary of the comparison of the heavy metals concentration average and standard deviation that samples as compared with the Standard Concentration on Ambient Air.

Table No. 4: Concentration of Heavy Metal in (mg/L) using ICP-OES.

Sample ID	Elements Concentration in ppm (µg.L^{-1})					
	As	Cd	Cr	Pb	Hg	Zn
S-1	LDL	LDL	0.106	0.010	0.007	0.222
S-2	LDL	LDL	0.052	LDL	0.010	0.102
S-3	LDL	LDL	0.037	0.021	0.014	0.245
S-4	LDL	LDL	0.030	LDL	0.011	0.100
S-5	LDL	LDL	0.027	LDL	0.008	0.145
S-6	LDL	LDL	0.039	0.007	0.015	0.209
S-7	LDL	LDL	0.020	LDL	0.009	0.075
S-8	LDL	LDL	0.028	LDL	LDL	0.115
S-9	LDL	LDL	0.040	LDL	0.012	0.127
S-10	LDL	LDL	0.022	LDL	0.012	0.047
S-11	LDL	LDL	0.039	LDL	0.010	0.111
S-12	LDL	LDL	0.013	LDL	0.009	0.068
S-13	LDL	LDL	0.023	LDL	0.032	0.050
S-14	LDL	LDL	0.039	0.185	0.014	0.113

LDL: Lower than detection limit

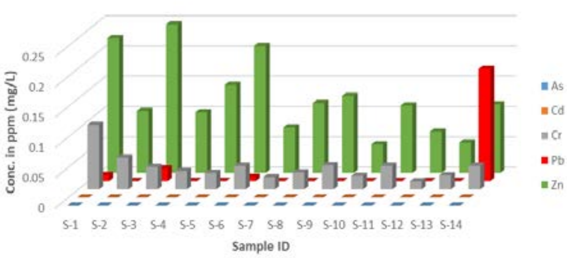

Figure No. 2: Concentration of Heavy Metal (µg.L^{-1}) in different samples

Lead Concentrations

The monitoring of Pb concentration becomes essential because it is widely distributed. According to both NEPC and AAQC the Pb content in the air may not exceed 0.500 µg.L-1. Pb concentrations in this study were in the 0.001– 0.185 µg.m-3 range. The whole investigated samples had values in the range. But the sample (14) was near crude heavy vehicle area had five times higher values than other samples.

Chromium Concentrations

National Research Council, Food and Nutrition Board recommended the daily intake of Cr which is between 50–200 µg/L-1 **(Bratakos *et al.*, 2002).** And Texas Commission on Environmental Quality (TCEQ) is 0.01 µg/L-1. The estimated levels of Cr found in the samples of the study ranged from 0.013–0.10 µg/L-1. The values of (S1 and S12) are found to be more than the surface guideline provided by the (TCEQ).

Zinc Concentration

Zinc is a nutritionally essential metal, and deficiency could cause severe health consequences, the consequences of Zinc deficiency in a huge spectrum of clinical effects depending on age, stage of development, and deficiencies of associated metals. Excessive exposure to zinc is relatively uncommon and occurs only at very low levels **(Bakircioglu *et al.*, 2011).** 60 mg of zinc is considered as a maximum acceptable daily intake **(Joint FAO/WHO, 1999).** In this study, the value of zinc of the samples is lower compared to WHO's value for daily intake, which is 0.050 – 0.240 µg.L-1.

Cd and Arsenic Concentration

Cadmium and Arsenic are toxic metals causing renal tubular dysfunction and bone toxicity at low exposure levels, such as in the general nonsmoking population. In addition to that, recent studies suggest a correlation between hormone-related cancers and elevated cadmium exposure, e.g. breast cancer **(Minh *et al.*, 2012)** as well as effects on neurodevelopment **(Ciesielski *et al.*, 2012).** Both of them in all air samples analyzed in this study were lower than the detection limit.

Conclusion

The present study was carried out for the first time in Kalar City. Herein, the result of the analysis reveals that the concentrations of Cd and As are lower than the detection limit, while, Pb, Zn, Cr are less than the normal range. In conclusion, the sample (S-1 and S-3) contain the highest concentration of heavy metals especially concentration of Chromium and Lead near to the Ambient Air Quality Criteria Act 1994 (AAQC), Texas Commission on Environmental Quality (TCEQ), National Environment Protection Council (NEPS) specification for heavy metals in air atmospheric this due to a large number of cars passing through the urban site and the variations in the source strengths (distances from the sources and relative importance of local sources). While the sample (S-8 and S-12) which contain the lowest concentration of heavy metal.

Finally according to DIRECTIVE 2008/50/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 May 2008 on ambient air quality and cleaner air the Kalar City air is clean and safe for humans.

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